Materials Letters 65 (2011) 1371–1374

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Aniline- and *N*,*N*-dimethylformamide-assisted processing route for graphite nanoplates: intercalation and exfoliation pathway

Chellachamy A. Amarnath [a], Chang Eui Hong [b], Nam Hoon Kim [c], Bon-Cheol Ku [d], Joong Hee Lee [a,b,c,]*

[a] *Department of BIN Fusion Technology (WCU Program), Chonbuk National University, Jeonju, Jeonbuk 561–756, South Korea*
[b] *BIN Fusion Research Center, Department of Polymer & Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk 561–756, South Korea*
[c] *Department of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju, Jeonbuk 561–756, South Korea*
[d] *Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Woanju, Jeonbuk, 565–902, South Korea*

ARTICLE INFO

Article history:
Received 16 October 2010
Accepted 1 February 2011
Available online 18 February 2011

Keywords:
Graphite nanoplates
XPS
Carbon materials
Intercalation
Exfoliation

ABSTRACT

Aniline-intercalated graphite nanoplates (AGNPs) were synthesized directly from graphite *via* an intercalation and exfoliation pathway using aniline as the intercalating agent and *N*,*N*-dimethylformamide (DMF) as the exfoliating agent. Thus, the obtained AGNPs were dispersible in various organic solvents like ethanol, isopropanol, chloroform, and benzene. This process is convenient, readily scalable and eco-friendly. We found that π–π interactions and the charge transfer complex formation between aniline and graphite nanoplates (GNPs) are responsible for the dispersion of AGNPs in organic solvents. The formation of AGNPs was confirmed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), X-ray photoelectron (XPS), Raman and UV–Visible spectroscopic measurements.

1. Introduction

Low density, high aspect ratio materials are desirable for producing nanocomposites. The idea is to reinforce the polymer matrix while preserving its lightweight assets. A perfect nanocomposite material requires a high aspect ratio of at least 500 [1]. Layered silicates [2–8], carbon nanotubes [9–11], and graphite nanoplatelets [12,13] are all currently under intense exploration as reinforcing agents. Graphite is a layered material made up of sheets of carbon that are one atom thick. By separating the graphite layers through intercalation and exfoliation, thin nanoplates can be formed that possess a high surface area and satisfy the high aspect ratio criterion needed for high strength composites. The theoretical surface area of a graphite sheet is 2630–2965 m^2g^{-1} [14,15]. Inagaki et al. [16] and Beguin et al. [17] have reported the synthesis of donor-type graphite intercalation compounds formed with alkali metals dissolved in tetrahydrofuran. Kaner et al. synthesized graphite nanoplatelets by alkali metal intercalation, followed by ethanol exfoliation and microwave drying. This process employed a hazardous material (NaK_2), which is highly flammable, and afforded nanoplates with thickness of 2–10 nm [18]. Herein, we report a simple approach to prepare AGNPs directly from graphite. We utilize aniline to intercalate between graphite and DMF to exfoliate the aniline-intercalated graphite to form AGNPs. The formation of AGNPs was confirmed using TEM, HRTEM, SAED, XRD, XPS, Raman and UV–Visible spectroscopic measurements.

2. Experiments

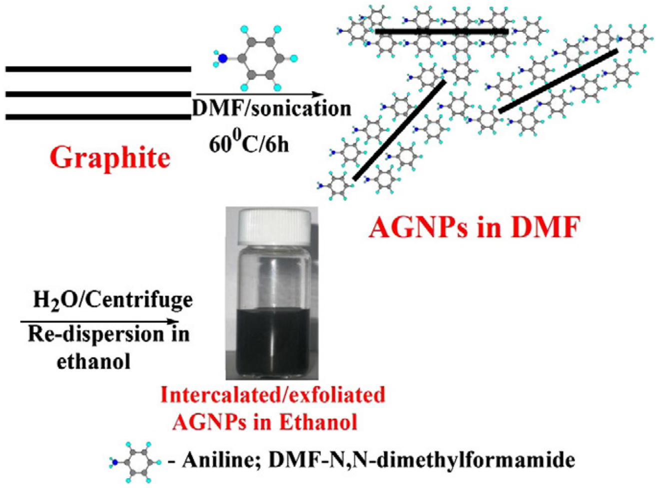
Graphite, aniline, and other chemicals were purchased from Sigma-Aldrich and used without further purification. In brief, 10 mg of graphite was sonicated with 5 ml of aniline for 3 h and 5 ml of DMF for another 3 h at 60 °C. The reaction mixture was left to stand overnight to allow unstabilized graphite to settle. The supernatant was decanted, mixed with water for AGNPs precipitation, and centrifuged at 5,000 rpm for 20 min. The resultant solution obtained could then be re-dispersed into organic solvents such as ethanol, isopropanol, chloroform, and benzene. The resulting dispersion contains 0.5 mg of AGNPs in 1 ml solvent. The same synthesis procedure was carried out without aniline and the reaction did not afford the dispersion.

TEM, HRTEM, and SAED measurements were carried out on a Tecnai G2 F30, FEI, (Japan) TEM at 200 kV. XPS analysis was carried out in AXIS-NOVA, Kratos Analytical Ltd, UK. The UV–visible spectrum of the AGNPs in ethanol was recorded using an UVS-2100 SCINCO spectrophotometer. XRD study was employed with a D/Max 2500 V/PC diffractometer (Rigaku Corporation, Japan). Raman spectra were recorded in a Nanofinder 30 confocal Raman Microscope (Tokyo instruments).

---

* Corresponding author at: BIN Fusion Research Center, Department of Polymer & Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk 561–756, South Korea. Tel.: +82 63 270 4803; fax: +82 63 270 2341.
E-mail address: jhl@jbnu.ac.kr (J.H. Lee).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.02.005



Scheme 1. Synthesis of AGNPs.

3. Results and discussion

Scheme 1 shows the synthesis of the AGNPs. During the synthesis, the aniline moieties were intercalated into the graphite to form aniline-intercalated graphite. In presence of DMF, the aniline-intercalated graphite was exfoliated to form AGNPs dispersion in DMF, along with unused aniline. By treatment with water, the unused aniline and DMF were removed from the AGNPs–DMF dispersion to form AGNPs precipitate. Thus, the obtained AGNPs precipitate was easily dispersible in ethanol, isopropanol, chloroform, and benzene by sonication. We found that π–π interactions [19] and charge transfer complex formation by aniline and GNPs could account for the dispersion of the AGNPs into organic solvents.

Fig. 1(a) and (b) show the TEM image of the AGNPs. In Fig. 1(a), AGNPs with smooth and flat surface of a few hundred square nanometers were observed. Furthermore, from Fig. 1(b), the most transparent and featureless portions of the AGNP, indicated by the arrow mark are likely monolayer GNPs. As reported earlier [20], corrugation and scrolling are intrinsic to GNPs since the thermodynamic stability of the 2D membrane results from microscopic crumpling *via* bending or buckling. Fig. 1(c) shows an HRTEM image of the cross sectional view of the AGNPs which are composed of five layers with the ordered graphite lattices. The increase in d-spacing around 0.43 nm from 0.33 nm of graphite was observed in the AGNPs (Fig. 1(c)), and proved the intercalation of aniline in the GNPs. SAED of this region along the [001] zone axis is shown as the inset in Fig. 1(c). The well-defined diffraction spots confirm the crystalline structure of the AGNPs. The combination of intercalated and exfoliated graphitic structures has been clearly revealed in these figures.

Fig. 2(a) shows the XPS C1s spectra of the graphite and AGNPs. Fig. 2(a) shows the peak at 285.9 eV with a well-known asymmetric shape line attributed to the sp^2 hybridized C1s peak of the graphite [21]. After the intercalation of aniline in the GNPs, the peak position of C1s spectra was observed at 285.6 eV (dotted line in Fig. 2(a)). After deconvoluting the peak at 285.6 eV, two peaks at 284.9 and 285.3 eV were detected for C=C/C–C and C–N, respectively (Fig. 2(b)). These peaks prove the presence of sp^2 hybridized carbon atom and non-covalently bonded aniline in the AGNPs [22,23]. In addition, the peak for nitrogen appeared at 399.9 eV (Fig. 2(c)) due to the aniline nitrogen [23], which is non-covalently bonded to the AGNPs. These peaks at 399.9 eV (nitrogen) and 285.3 eV (C–N) are evidence for the formation of AGNPs. The shape-up peak at around 289 eV for AGNPs proved the presence of π–π interactions [24] between the GNPs and aniline molecules and thus indicated the formation of AGNPs by intercalation of aniline in the GNPs.

A UV–visible spectrum of the AGNPs in ethanol is shown in Fig. 3(a). Compared to the pristine aniline (absorption at 320 nm), the new peaks were found near 350 (strong) and 530 nm (weak) for AGNPs. This is due to the formation of a charge transfer complex formation between the GNPs and aniline. This could be similar to the charge transfer complex mechanism of carbon nanotubes (CNT) and

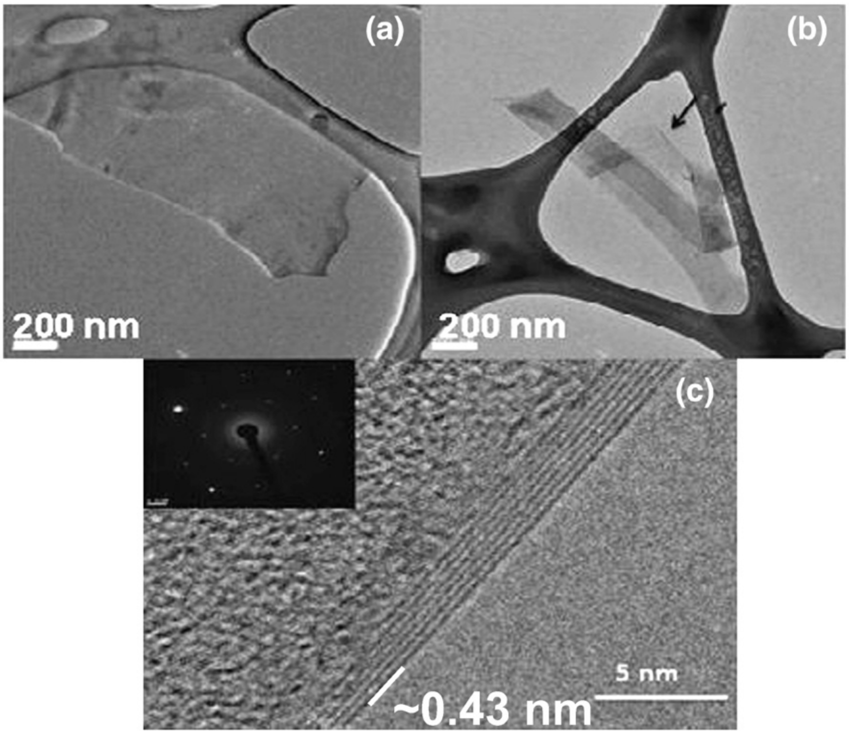


Fig. 1. TEM images of the (a) AGNPs, (b) monolayer present in AGNPs labeled by arrow and (c) HRTEM image of the AGNP edge; the inset in (c) is a typical AGNPs SAED pattern.